

*Thorianite, a New Mineral from Ceylon.*

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The mineral which forms the subject of this paper was collected in Ceylon during the progress of the mineral survey of the island, which was commenced in 1903 under Professor Dunstan's supervision, with the principal object of determining the extent to which economic minerals, such as graphite, mica, etc., occur, and if possible of discovering other minerals of commercial importance. The minerals collected by Mr. A. K. Coomaraswamy and Mr. James Parsons, the officers entrusted with the survey in Ceylon, are submitted to examination and analysis in the Scientific and Technical Department of the Imperial Institute, and are subsequently subjected to such technical trials as may be necessary in order to ascertain their precise uses and to determine their value.

Among the materials thus received from Ceylon at the Imperial Institute was a small quantity of a heavy black mineral occurring chiefly in small roughly cubical crystals. This mineral was, in the first instance, furnished to the officers of the mineral survey by Mr. W. D. Holland, who believed it to be uraninite or pitchblende. He had previously sent specimens to several persons in this country under this name.

A chemical examination of the small specimen received at the Imperial Institute showed, however, that the mineral contained a large proportion of thorium in the form of the dioxide (thoria) and only a small proportion of uranium. It was evident that this was a new mineral chiefly composed of uncombined thoria ( $\text{ThO}_2$ ). Pending the arrival of more material to enable a further examination of its properties to be made, a preliminary account of its composition and properties was communicated by one of us to 'Nature,'\* and the name *thorianite* was suggested for the substance, which contained at least 75 per cent. of thoria.

It was also stated that the mineral was radio-active and that it apparently contained helium, points which would be made the subject of further investigation.

The publication of these results was followed by a communication to 'Nature'† from Sir W. Ramsay, who announced that he had purchased 6 cwt.

\* March 30, 1904, p. 510.

† April 7, 1904, p. 533.

of the mineral from Mr. Holland some months previously and had been engaged in its examination. He was unable to confirm the statement that it contained thoria, but announced that it had furnished considerable quantities of helium. In a second communication to 'Nature'\* Sir W. Ramsay modified the statement he had previously made that the mineral contained practically no thorium.

Further small supplies of the mineral having since been received at the Imperial Institute, we have been enabled to confirm the conclusion first arrived at that the substance is chiefly composed of thoria, and we now desire to bring before the Royal Society an account of this remarkable new mineral for which the name thorianite is appropriate.

A general account of the composition, properties, and uses of thorianite is included in Professor Dunstan's official 'Reports on the Results of the Mineral Survey in Ceylon, 1903-4,' which was issued as a Parliamentary Paper (Cd. 2341) in January, 1905.

#### *Occurrence of Thorianite in Ceylon.*

The following account of the occurrence of the mineral, at first supposed to be "uraninite," has been given in official reports by Mr. A. K. Coomaraswamy, B.Sc., the Director of the Mineral Survey in Ceylon.

"Mr. Holland of Dikmukulana has for long taken an interest in local mineralogy, amongst other things obtaining specimens of 'nampu' (gem-bearing gravels) from as many localities as possible by offering a small reward to the native 'gemmers' who bring it. It is difficult to persuade the native that gems are not required or to get him to reveal the true source of 'nampu.' These difficulties overcome, the examination of 'nampus' is an ideal method of gaining a knowledge of heavy minerals of any district. Early in 1903 Mr. Holland obtained 'uraninite' amongst his samples and was gradually able to get as much as 6 cwt. brought to him along with other stuff. This material was sent to England and sold to Sir W. Ramsay at the rate of £50 for 6 cwt. Subsequently Mr. Holland induced a native to show him the source of the material, and finding that some quantity occurred, he took out a prospecting license in the full belief that the locality was Crown land.

"Thorianite, together with a mineral regarded as thorite, and a number of other heavy minerals, is found near Kondurugala, Bambarabotuwa, Province of Sabaragamuwa. The principal deposit occurs in and near the bed of the upper part of the Kuda Pandi-oya, a small stream, which at first occupying a small north-west and south-east strike valley north of the Hopewell-Hapugastenna bridle path, turns through nearly a right angle and joins the Maha Pandi-oya a little below the same path. In the bed of the Kuda Pandi-oya, and in a small 'deniya' swamp just below the swamp, the thorianite is to be obtained in considerable abundance. It could not be discovered *in situ*, but it can hardly be doubted that it is derived from some rock outcropping not far distant from the highest part of the little

\* April 14, 1904, p. 559.

stream; the stream is so small that after a few days of drought (not very usual in this wet district) no running water is met with above the camp. The matrix is no doubt a rock of granitic type similar to those containing zircon, allanite, etc., which have been met with elsewhere in the Balangoda district, intrusive in the Charnockite series, and classed as belonging to the Balangoda group. Of these rocks the largest exposure (a narrow lenticular mass two miles or more in length) is that of zircon granite on Massena estate (six miles);\* the rock consists of feldspars, quartz, biotite, zircon, and ilmenite; smaller exposures of zircon granite are found on Herimitigala (eight miles) and Hopewell estates (15 miles); at Denegama bridge, on the road between Balangoda and Belihul-oya, and near the 91st milepost on the same road. There are also similar granites without accessory minerals exposed—*e.g.*, on the main road about a mile below Balangoda. The allanite-granite, or pegmatite, is best seen on Lower Denegama estate, where it occurs as a dyke 3 or 4 feet thick, forming a conspicuous ledge in the bed of the stream which runs through that part of the estate. The rock is composed of feldspars (chiefly orthoclase), quartz, biotite, and allanite. The allanite forms thin tubular idiomorphic and larger irregular crystals, the biggest having a greatest diameter of 3 inches. Almost identical rocks occur (1) in the Weweldola on Dikmukulana estate (11 miles), and (2) at Weligepola (9 miles). It is important to observe that a pegmatite rock, composed mainly of pink orthoclase, quartz, and biotite, with accessory apatite, tourmaline, ilmenite, etc., has been observed on Ambalawa estate, Gampola,† containing, in addition to the above-named minerals, a few cubic crystals of a black mineral at first regarded as uraninite, but which is almost certainly thorianite.

“To return to the Kondurugala locality, the thorianite is probably derived from a granitic rock with no very large outcrop, but in which it occurs in considerable abundance; perhaps together with the zircon, thorite and ilmenite, which quite possibly, however, occur separately in other rocks of a similar character. The outcrop of this rock could not be discovered owing to the dense jungle and thick soil and landslips; rock (mainly decomposed granulite) is indeed exposed at several points in the beds of the Kuda Pandi-oya and of the small streams joining it, but any search for the outcrop of a particular rock in the adjoining jungle could only be expected to succeed at the cost of a large expenditure of time and money, and might even then result in failure.

“There is a large area, including at least the whole of Sabaragamuwa and parts of the central, western, and southern provinces, wherein this or other rare heavy minerals may be looked for.

“It is unlikely that any very extensive deposit of any of these rare heavy minerals will be found, but they may be expected to occur at various points in moderate amounts. In the Kuda Pandi-oya valley a total of 5 tons might, perhaps, be obtained; from the Alupola-dola or the Kuda-oya I doubt if half a ton could be profitably extracted, but these estimates are quite uncertain. The Gampola occurrence is quite without commercial value. The total amount actually obtained in Bambarabotuwa, so far, does not exceed 15 cwts. In the

\* The distances are quoted from Balangoda.

† ‘*Spolia Zeylanica*,’ vol. 1, part iv, 1904.

immediate neighbourhood of Kondurugala the Walaweduwa jungle seems the most favourable district for investigation. An examination of the Ratganga valley towards the west showed that thorianite is absent there, and that even zircon is very scarce; but on the north-east one or two heavy minerals not yet determined were actually obtained in the southern part of the Walaweduwa Crown Forest Reserve, and further work on that side of Kondurugala might be useful. It must be mentioned, however, that the district is a very wet one, the jungles swarming with leeches; it is also very inaccessible, provisions and camping effects having to be carried fully 20 miles from Balangoda. Camping in these jungles is absolutely useless except in fine weather; and in the absence of a detailed map observations cannot be very accurately set down.

"Since August, 1904, a small deposit of the mineral provisionally identified as thorite was discovered at Durayakanda, South of Gilimale, about six miles from Ratnapura.

"A further amount of 1,200 lb. of thorianite has since been obtained from Bambarabotuwa."

#### *Description of Thorianite.*

Thorianite, as it occurs naturally, is often associated with other minerals, and is not easy to obtain in a completely separate condition.

Dr. J. W. Evans has made a preliminary examination of the crystallographic characters, and intends to further study this subject. It may be stated now that the mineral occurs in small cube-like crystals up to nearly a centimetre in diameter, the largest, so far seen, measuring rather more than 8 mm. In most specimens the colour is a dull grey or slightly brownish black, but those crystals which have not suffered from attrition in the streams are a jet black with a bright resinous or pitchy lustre. The difference may be attributed partly to the grinding of the surface, and partly to superficial chemical changes. The mineral thus differs from uraninite or pitchblende which usually occurs massive, and not obviously crystalline. The streak furnished by uraninite is brown with a tinge of green.

By transmitted light the mineral is opaque except in thin sections.

The double refraction is very low. The refractive index probably exceeds 1.8.

The only faces that are ordinarily developed on the crystals of thorianite are apparently those of the cube. These have a very uneven surface, especially in specimens that have not suffered much from attrition or alteration. This character of the surface is mainly the result of the development of a number of small vicinal faces. In some cases larger faces of similar character are present, meeting at very obtuse re-entrant or salient angles, and reminding one of those seen in some crystals of fluorspar. In other crystals the faces show a more or less irregular curvature.

The indefinite character of the surface prevents any accurate determination of the angles. The goniometric readings vary 2 or 3 degrees on either side of 90 degrees, according to the portions of the surface from which the image is reflected, but there is in most cases no satisfactory evidence that the faces as a whole are not virtually at right angles. Some crystals, however, appear to be distorted and have angles differing from a right angle by as much as 5 degrees or even more.

Occasionally twin crystals are met with and these are of some interest. They are interpenetrant twins on a face of the octahedron as twinning plane, and one of the diagonals of the cube as twinning axis, exactly similar to those of fluorspar. As in the case of that mineral the coigns of one cube project as pyramids on an isosceles triangular base on the face of the other. Sometimes the compound form is almost completely regular, four edges of each cube meeting at one point or approximately so at both ends of the common diagonal that forms the twinning axis; at other times the composition is more irregular, and a number of coigns project from the faces of a cube in such a manner that though the faces of one coign are parallel to those of another, they are not in the same plane. In these forms the twinning axis and plane are the same for all the coigns, even when there is more than one projecting from the same face, the more acute point of the pyramid pointing to the coign of the cube from which the twinning axis emerges. The diagonal which constitutes this axis has therefore crystallographic characters different from those of the other three diagonals, about which this twinning cannot apparently take place, and the symmetry of the crystal must be considered as rather rhombohedral than cubic, although the angles are apparently right angles. The same considerations would apply to fluorspar, in which case the essentially rhombohedral character of its symmetry is confirmed by the occurrence of crystals in which only those faces of the four-faced cube or tetrakis hexahedron  $\{310\}$  are developed, in which the finite intercepts are of opposite signs. These faces may be represented by the symbol  $\{3\bar{1}0\}$ , and are those which bevel the edges that do not pass through the coigns at the ends of the unique diagonal. They together form a scalenohedron, which is in fact the scalenohedron  $\{13\bar{4}2\}$  of the rhombohedral system, assuming the cube as the fundamental rhombohedron.\*

A similar scalenohedron  $\{2\bar{1}0\}$  or  $\{12\bar{3}1\}$  is repeatedly met with in crystals of halite.†

\* 'Lehrbuch der reinen und angewandten Krystallographie,' 1830, p. 178, fig. 572.

† F. von Kobell, "Über Merkwürdige Krystalle von Steinsalz," 'Journal für praktische Chemie,' 1861, vol. 84, p. 420; K. André, "Über Steinsalz Krystalle von hexagonal-rhomboëdrischer Pseudosymmetrie aus Sicilien," 'Centralb. für Mineralogie,' etc., 1904, p. 88.

It is interesting to notice that chabazite, which is cubic in general appearance, but really rhombohedral, having its angles differing from right angles by nearly 5 degrees, twins in exactly the same manner as fluorspar and thorianite.

The inference that thorianite is essentially rhombohedral in character is confirmed by the observation that in sections cut perpendicular to the twinning axis, the substance is practically isotropic.

Thorianite shows no definite cleavage, but the mineral is traversed by irregular cracks which appear to follow the direction of the basal plane more frequently than any other. On fracture, it shows an irregular surface, which is more or less conchoidal on a small scale.

The hardness of the mineral is nearly 7, which distinguishes it at once from uraninite with a hardness of 5.5.

Under the blow-pipe thorianite is infusible. It decrepitates, and if raised to a sufficiently high temperature, is highly incandescent.

It is sometimes associated in rolled fragments with a smooth, yellow-brown, apparently amorphous material, of hardness 6, which envelopes it or forms a rounded deposit on its faces. This substance is reddish-yellow in colour when viewed in thin sections by transmitted light. Zircon also sometimes occurs intergrown with thorianite.

The density of different specimens of thorianite varies between 8 to 9.5 and 9.7. The higher numbers probably represent the density of the actual mineral, which in some cases exhibits cavities partially filled with a yellow ochreous material and also inclusions of zircon, one of the minerals generally associated with thorianite, and these associated minerals, especially those which contain thorium, will be investigated if a sufficient quantity can be obtained separated from thorianite.

The mineral is easily powdered and then dissolves readily in strong nitric acid or in diluted sulphuric acid, with evolution of a gas which is chiefly helium. Thorianite is scarcely attacked by hydrochloric acid.

Thorianite is highly radio-active, and, in fact, may prove to be one of the most radio-active of minerals. The cause of this radio-activity is referred to below.

#### *Composition of Thorianite.*

The methods used in determining the composition of thorianite are founded on those suggested by Glaser\*, Meyer and Marckwald†, Fresenius and Hintze‡, and Benz§.

\* 'Zeits. Anal. Chem.,' 1897, vol. 36, p. 213.

† 'Ber.,' 1900, vol. 33, p. 3003.

‡ 'Zeits. Anal. Chem.,' vol. 35, p. 343.

§ 'Zeits. Ang. Chem.,' 1902, p. 297.

The results are shown in the table on p. 261, which includes the data obtained from three separate specimens, numbered I, II, and III.

In the estimation of the metals, 2 grammes of the finely powdered mineral were dissolved in about 15 c.c. of nitric acid of specific gravity 1.4, and after decomposition was complete the solution was diluted and filtered. The insoluble residues in specimens II and III were very small, and were treated with hydrofluoric acid to estimate silica. In I the residue chiefly consisted of zircon which was fused with potassium hydrogen sulphate to extract zirconia, and the residue treated as before with hydrofluoric acid to estimate silica. Except for this associated zircon, no zirconia was found in the mineral.

The acid filtrate from the insoluble residue was diluted to about 300 c.c. and 5 c.c. of hydrochloric acid added. Hydrogen sulphide was then passed through the liquid to precipitate lead which was finally weighed as sulphate. The filtrate was boiled to remove hydrogen sulphide, and oxidation of the last traces of this substance effected with bromine water. To the hot acid solution, amounting to about 350 c.c., excess of ammonium oxalate was added, and the precipitate of oxalates of thorium and cerium, etc., allowed to settle overnight and then filtered. The filtrate was evaporated to dryness and treated with nitric acid to destroy oxalic acid, and diluted with water. The calcium and magnesium were separated from other metals by precipitating the latter with ammonia and ammonium chloride. This precipitate was dissolved in hydrochloric acid, excess of acid neutralised, and the solution diluted to 500 c.c. A few drops of solution of sodium sulphite were added, and the liquid boiled to precipitate any titanous acid. No titanium was, however, present. The liquid was evaporated, and the iron oxidised with a few drops of nitric acid. The liquid was neutralised with a few drops of ammonia, and finally excess of ammonium carbonate added. The carbonates first precipitated were re-dissolved on further addition of the reagents, showing the absence of alumina. The iron was separated as sulphide. The filtrate was boiled, acidified with hydrochloric acid, and again boiled to remove all the carbon dioxide. The uranium in solution was precipitated with ammonia, and finally weighed as uranous-uranic oxide  $U_3O_8$ .

The precipitate containing the oxalates of thorium and cerium, etc., was dried, and the oxalates were then decomposed by nitric acid, and the metals obtained in solution as nitrates. After diluting to 250 c.c., sodium thio-sulphate was added to the slightly acid boiling liquid till no further precipitate of thorium salt was obtained. The liquid was boiled for a short time, the precipitate filtered off and dissolved in hydrochloric acid, and the

operation twice repeated to completely separate the cerium. To the united filtrates ammonia was added, and the precipitate of hydroxides of the cerium, etc., containing a little thorium and any yttrium present, was dissolved in hydrochloric acid, and the trace of thorium precipitated as above described from a small bulk of liquid. The thorium precipitates were dissolved in hydrochloric acid, and the thorium re-precipitated as hydroxide and finally weighed as the dioxide  $\text{ThO}_2$ . The filtrate from precipitation of the cerium earths with ammonia contains lime if such were present in the original mineral. This was separated as oxalate and weighed as oxide.

Determinations of the equivalent of thorium made with the precipitated dioxide obtained in the course of the analysis of the third specimen (see p. 261) by conversion into the sulphate gave 57.25, corresponding with an atomic weight of 229. The accepted atomic weight of thorium, relative to hydrogen taken as 1, is 230.8.

The solution from which thorium had been thus removed, containing cerium and the associated earths, including any yttrium, was treated with ammonia; the precipitate dissolved in dilute sulphuric acid, and the solution, after neutralisation, saturated with potassium sulphate. No yttrium was found in the filtrate by dilution and addition of ammonia.

The double sulphates of potassium with cerium, and of the associated metals lanthanum and didymium, were warmed with ammonia solution, by which means the earths were obtained as hydroxides. These were dissolved in hydrochloric acid and re-precipitated by potash solution. The hydroxides were washed by decantation, a little potash solution added, and chlorine gas passed until the liquid was saturated. The lemon-coloured hydrated ceric oxide was filtered off, re-dissolved, and re-precipitated as hydroxide, and the cerium weighed as the dioxide  $\text{CeO}_2$ . The filtrate containing lanthanum and so-called didymium was acidified with hydrochloric acid, boiled to remove chlorine, and the earths precipitated with ammonia and weighed as the oxides.

The uranous oxide ( $\text{UO}_2$ ) was separately estimated by Hillebrand's method as follows:—One or 2 grammes of finely powdered mineral were introduced into a stout tube together with 20 to 30 c.c. of dilute sulphuric acid, consisting of one part of acid to five parts of water. The air was then displaced by carbon dioxide, the tube sealed off, and then heated to  $180^\circ \text{C}$ . for several hours till decomposition was complete. The solution obtained was diluted with recently boiled water, and the uranous sulphate titrated with potassium permanganate.

The method adopted for the determination of helium and associated gases consisted in decomposing the mineral by means of dilute sulphuric acid



consisting of one part of acid to five parts of water.\* Ten grammes of the powdered mineral were used, and the gas collected in a gas burette over mercury with the usual precautions. The mixture was heated at 100°. Decomposition at this temperature was almost complete in one day, but the experiment was allowed to continue for two days to ensure the liberation of all the gas.

The gas collected amounted to 105 c.c. at standard temperature and pressure, which corresponds to 10·5 c.c. of gas, chiefly helium, from one gramme of thorianite.

Analyses of Thorianite.

	I.	II.	III.
	Per cent.	Per cent.	Per cent.
Soluble in nitric acid—			
Thorium dioxide .....	72·24	76·22	78·86
Uranium „ .....	11·19	12·33	6·03
Uranium trioxide .....	—	—	9·07
Cerium dioxide.....	6·39	8·04	1·02
Lanthanum and didymium oxides ...	0·51		
Yttrium oxide .....	—	—	—
Lead „ .....	2·25	2·87	2·59
Ferric „ .....	1·92	0·35	0·46
Calcium „ .....	—	—	1·13
Helium .....	—	—	0·39†
Titanium dioxide .....	—	—	—
Phosphoric oxide .....	—	—	trace
Insoluble in nitric acid—			
Zirconium oxide .....	3·68	—	} 0·20
Silica .....	1·34	0·12	
Residue from fusion with potassium hydrogen sulphate .....	0·41	—	—

Of the three specimens of thorianite analysed the first was too small to admit of any treatment to separate associated minerals, and proved to contain associated zircon. Specimens II and III were separated as far as possible from extraneous minerals, and represent a nearer approach to the single mineral. The highest amount of thoria yet found is nearly 79 per cent., which shows that thorianite is the richest mineral in thoria at present known.

\* Hillebrand, *loc. cit.*

† If the whole of the gas is calculated as helium.

*Constitution of Thorianite.*

From the analytical results, it will be seen that the constituents other than thoria show, as was to be expected in a mineral of this character, some variation. In Nos. I and II cerium dioxide occurs up to the extent of 8 per cent., while in No. III it becomes almost insignificant. The uranium appears to occur in the condition of both uranous and uranic oxides. It is, however, intended to further investigate this question, since the presence of uranic ochre on the surface of some specimens would indicate that the mineral may have suffered considerable superficial oxidation, and that crystals may be found containing a much smaller proportion of uranic oxide. Of the other oxides present, zirconia in the insoluble residue may be safely classed as an impurity arising from zircons which are invariably found with thorianite, sometimes included within the crystalline thorianite. Silica and ferric oxide may be neglected as contaminations. Leaving out of consideration for the present the oxides of lead and calcium (not a constant constituent) the mineral consists of a large amount of oxide of thorium and a small amount of oxides of uranium, with a smaller and variable amount of cerium oxide, the precise significance of which is at present doubtful.

In the original condition the uranium may have existed entirely as dioxide. There can be little doubt that the dioxides of thorium and uranium, as well as certain of the salts of these metals, are isomorphous. In nature these oxides have not been found in a pure crystalline state, but crystals of each have been obtained artificially. Crystalline thoria was obtained by Troost and Aouvrard\* whilst studying the relation between the double phosphate of potassium and thorium and that of potassium and zirconium. The phosphates were first obtained by adding to fused potassium orthophosphate, thoria, thorium phosphate or anhydrous thorium chloride. On raising the double phosphate to such a temperature that both alkali and phosphoric acid were volatilised, thoria was obtained in crystals belonging to the cubic system; the cuboctahedron and rhombic dodecahedron being the forms observed.† Again, uranium oxide was first obtained in an octahedral form by Wohler by heating a mixture of uranium oxychloride with sodium chloride and ammonium chloride.‡ Later, Hillebrand repeated the experiment, and obtained practically pure uranium dioxide in black octahedral crystals of a specific gravity of about 11.§

The hydrate of thorium sulphate  $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$  is also, according to

\* 'Comptes Rendus,' 1886, vol. 102, p. 1422.

† *Loc. cit.*

‡ 'Liebig's Annalen,' 1842, vol. 41, p. 345.

§ 'Zeitschrift für Anorg. Chemie,' 1893, vol. 3, p. 243.

Rammelsberg,\* monoclinic in crystalline form and isomorphous with the corresponding hydrate of the uranium salt  $U(SO_4)_2 \cdot 9H_2O$ .

Our analyses of different specimens of thorianite are hardly sufficiently numerous to enable us to conclude that the oxides of thorium and uranium bear a definite relation to one another in the mineral. It seems probable that the mineral belongs to the class of substances known as isomorphous mixtures of which the simple form would be represented by the formula  $XO_2$  where X represents a tetravalent element the dioxide of which crystallises in the isometric system the extremes of which would be  $UO_2$  and  $ThO_2$ .

Thorianite is evidently closely related to uraninite (pitchblende) in constitution. The crystalline form of the two minerals is the same and the constituents of both are similar. Hillebrand's analysis of the Branchville varieties of uraninite, which were stated to be nearly unoxidised, furnished 72.25 per cent. of uranium dioxide and only 13.27 of uranium trioxide.† Uranium dioxide very readily oxidises on exposure to air, and it was only by completely excluding the air that Hillebrand succeeded in obtaining the pure oxide artificially. It is, therefore, certain that the natural varieties of the oxide so far examined must have suffered alteration and oxidation, and that originally their principal constituent was uranium dioxide. Most of the massive varieties of uraninite are very impure, and this may account in a large measure for the presence of many oxides in this mineral which appear to have very little in common with the principal constituents. Lead oxide is apparently generally present in thorianite. It occurs in small amount and may be combined as uranate. In the case of thorianite the crystallographic examination has shown that the mineral has crystallised with difficulty, and that it is more or less contaminated with those minerals which crystallised at the same time, as well as with impurities contained in the magma from which crystallisation occurred.

As far as the present investigation has gone it appears probable that thorianite is isomorphous with uraninite, and that in the thorianite of Ceylon some of the thoria is replaced by the corresponding uranium oxide. The evidence, however, is not sufficient to show whether this is a case of isomorphous mixture, as seems probable, or of true chemical replacement.

It is obvious that the mineral is one of exceptional interest, and that it presents many problems for investigation, among them being the question of the possible occurrence of small quantities of hitherto little known or unknown elements.‡ The material furnishes a satisfactory source of pure

\* 'Berl. Acad. Ber.', 1886, p. 603.

† 'Amer. Journ. Sci.', 1890, vol. 40, p. 384.

‡ Since this was written Hahn, in a communication to the Royal Society ('Roy. Soc.

thoria, a fact which is of commercial importance as well as of scientific interest.

We have shown that thorianite is chiefly composed of thoria, as at present understood. Baskerville believes that he has obtained evidence that the substance at present known as thorium is composed of more than one element, and that he has separated thoria into three oxides differing in density, and one of which is little, if at all, radio-active. These conclusions have, however, been called in question by Meyer and Gompertz,\* who assert that thoria shows no evidence of being other than a single substance.

Determination of the rate of decay of the radio-activity of thorianite made in Lord Blythswood's Laboratory by Mr. H. S. Allen have shown that this property of the mineral is probably consistent with the thorium, uranium, and small amount of radium present.

The radio-activity of the mineral was measured in a parallel plate apparatus, using sufficient material to entirely cover the lower plate. The observed rate of leak under these conditions was 6900 divisions per minute equivalent to a current through the apparatus of approximately  $5.5 \times 10^{-11}$  ampères. Thorianite is, therefore, somewhat less active than some of the specimens of pitchblende examined by Madame Curie, whose results with this mineral are as follows:—

Pitchblende from Johanngeorgenstadt.....	$8.3 \times 10^{-11}$ ampères	
„ „ Joachimsthal .....	$7.0 \times 10^{-11}$	„
„ „ Pzibram.....	$6.5 \times 10^{-11}$	„
„ „ Cornwall .....	$1.6 \times 10^{-11}$	„

A series of measurements of the rate of decay of activity of the emanation from thorianite have been made; 16.5 grammes of the mineral were heated in a hard-glass tube, and the emanation, previously dried over phosphorus pentoxide, collected in the testing vessel. It was set aside for 6 hours in order to allow the thorium emanation to decay, and then measurements of the activity were made daily.

The results showed that during the first four days the rate of decay was greater than that observed by Rutherford for radium emanation, but that after this period the rate of decay of activity became identical with that of radium emanation. It is probable that the greater rate of decay during the first four days was due to the presence of thorium “excited activity” which, (Proc., 1905) has announced the existence in thorianite of a small quantity of a new element, which produces the “thorium emanation.” This was separated from the 6 cwt. of the mineral referred to earlier in this paper. It must not be overlooked that the consignment, though apparently worked up as a whole, was doubtless a mixture containing several other minerals than thorianite.

\* ‘Ber.,’ 1905, vol. 3, p. 187.

according to Rutherford, decays to half value in the course of 11 hours, whereas the radium emanation falls to half value only in about 3·7 days.

These results clearly indicate the presence of radium emanation in the "total emanation" from thorianite, and that consequently this mineral must contain radium.

*Commercial Value of Thorianite.*

Owing to the increasing employment of thoria for the manufacture of incandescent gas mantles, the demand for minerals containing thorium has largely increased. The demand is chiefly met from the deposits of sand containing a small percentage of monazite (phosphate of the cerium metals and thorium) which occur in Brazil and in North Carolina. Owing to the foreign control of these sands, British manufacturers have experienced difficulty in manufacturing thorium compounds. Thorianite is, we believe, the first deposit of a thorium mineral to be discovered on British territory. Consignments of thorianite from Ceylon, containing about 70 per cent. of thoria, have been recently sold in this country at the rate of £1500 per ton.

For the manufacture of thorium compounds thorianite possesses the advantage, not shared by any known thorium mineral, of containing uncombined thoria, soluble in nitric acid with formation of thorium nitrate.

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